

Dynamic Model of Super-Arrhenius Relaxation Rates in Glassy Materials

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(Dated: September, 2004)

Abstract

We propose that the super-Arrhenius relaxation rates observed in glassy materials are determined by thermally nucleated rearrangements of increasing numbers of molecules at decreasing temperatures. In our model of this mechanism, string-like fluctuations in the neighborhood of shear transformation zones (STZ's) provide routes along which rearrangements can propagate, and the entropy associated with long enough strings allows the rearrangement energy to be distributed stably in the surrounding material. We further postulate that, at low enough temperatures, these fluctuations are localized on the interfaces between frustration-limited domains. Our result is a modified Vogel-Fulcher formula at low temperatures that crosses over to a simple Arrhenius law as the glass changes from being solid-like to liquid-like. To achieve agreement with experiment in the crossover region, we need to make what seem to us to be overly strong assumptions about the behavior of frustration-limited domains.

I. INTRODUCTION

Recent developments in the shear-transformation-zone (STZ) theory of amorphous plasticity [1, 2], especially its success in accounting for the behavior of bulk metallic glasses [3, 4], have prompted us to take a fresh look at the super-Arrhenius rates that characterize relaxation mechanisms in such materials. In our preceding STZ calculations, we have simply deduced these transition rates from experimental data and used them in predicting, for example, nonlinear plastic responses to driving forces. To make further progress, it will be useful to have a deeper understanding of the physical mechanism that underlies these rates or, at least, to have a physically motivated model to help us determine relevant parameters.

The main assumption of the STZ theory is that a deformable glassy material is fundamentally a solid in which irreversible molecular rearrangements occur at special sites – so called “flow defects” or “STZ’s.” [5, 6, 7, 8] The STZ theory therefore differs from mode-coupling theories [9, 10, 11], whose starting point is a liquid-like model. It also differs from earlier flow-defect theories of solid plasticity in that it attributes the super-Arrhenius behavior not to a temperature-dependent density of STZ’s (e.g. see [6, 12, 13, 14]) but, rather, to the temperature dependence of the rates at which the STZ’s transform. (For a recent summary of a wide variety of research in this and related fields, see [15].)

In the most recent version of the STZ theory [4], we characterized the configurational degrees of freedom, i.e. the inherent states of the system [16], by an effective disorder temperature; and we supposed that the STZ’s are especially deformable local density fluctuations that are far out in the wings of this effective thermal distribution. We are concerned specifically with the rates at which STZ’s switch from one orientation to another during shear deformations, the rates at which they are created and annihilated, and also the rate at which the effective temperature relaxes toward the temperature of the heat bath. More generally, we are interested in the spontaneous (that is, thermally assisted but not externally driven) mechanisms by which an amorphous solid makes transitions between its inherent states.

As has long been recognized in theories of glass dynamics (see especially Adam and Gibbs [17]), a qualitative reason why transition rates might become anomalously slow at low temperatures is that, as the temperature decreases, the statistically most probable transition mechanisms will be those that involve increasingly large numbers of molecules. When more molecules are participating, there will be larger numbers of routes by which the

transitions can occur and a correspondingly larger entropic reduction of the height of the activation barrier. To carry out an actual calculation, however, we must make a model of such a mechanism.

The model that we shall explore here is motivated in part by work of Glotzer and colleagues [18, 19], who discovered in molecular-dynamics simulations that transitions between inherent states in glass-forming liquids take place via motions of string-like groups of molecules. We postulate that, at temperatures low enough that most of the system is tightly jammed, localized molecular rearrangements might be entropically enabled by strings of small molecular displacements that distribute the disturbance throughout larger parts of the material. This picture may be loosely related to that of Cohen and Grest [20], who postulated that the statistics of free-volume fluctuations in glassy systems might be determined by the increase in communal entropy associated with the percolation of connected, possibly stringy, regions of low density. In granular materials, our hypothetical mechanism might be visualized as a kinetic fluctuation that allows molecules to undergo small displacements along a force chain.

For simplicity, consider first just the spontaneous STZ creation rate. It is useful to think of STZ creation as a thermally activated event in which the glassy analog of a vacancy and an interstitial first form, then move away from one another, and finally stabilize at an indefinitely large separation. More generally, the formation of an STZ is a spontaneous increase in the configurational disorder of the system, as measured by the intensity of density fluctuations. Suppose that, with a probability that we must calculate, the material in the neighborhood of this event contains a string of relatively loose molecules that provides a route along which the “vacancy” and the “interstitial” can propagate. Our strategy is to estimate the height of the free-energy barrier over which this system must fluctuate in order for it to become energetically favorable for the string to lengthen without bound. When that happens, we postulate that a dynamically stable STZ has formed, and that whatever excess energy was needed to cause the local rearrangement has been dissipated into the surrounding medium. In short, we propose to solve a nucleation problem where the reaction coordinate is the length of this string. The entropy associated with different string configurations is a measure of the number of routes across this energy barrier and, therefore (see [21]), reduces the free energy of the barrier for purposes of computing the nucleation rate. We present an elementary theory of this mechanism in Section II.

Our picture of localized, string-like fluctuations in an amorphous solid lends itself naturally to the description of glasses at temperatures low enough that the system retains most of its elastic properties, including its shear modulus. This is the region in which the behavior is markedly super-Arrhenius. The picture is not so natural, however, at higher temperatures where the material softens and undergoes an apparently smooth transition between solid-like and liquid-like states, and where the super-Arrhenius behavior reverts to relaxation with a temperature-independent activation energy. We cannot (yet) present a first-principles theory that spans these liquid-like and solid-like regimes. However, in Section III, we present what we believe is a plausible description of this “no-theory” region between solid-like and liquid-like glasses, and we show how such a semi-phenomenological analysis might account for experimental observations. As we shall see, our model contains too many adjustable parameters and other *ad hoc* features for the fit to experimental data to be convincing. However, our theory at least has the virtue that it allows us to assign physical meaning to its constituent parameters and may even be experimentally falsifiable; thus it may lead to productive new lines of investigation.

II. ELEMENTARY STRING MODEL

To describe the string model outlined in the preceding paragraphs, we let the string have length N in units of some characteristic molecular length, say, ℓ , and suppose that it occupies a region of size R in the neighborhood of the emerging STZ. The total excess free energy of the system consists of several parts, which we denote:

$$\Delta G(N, R) = \Delta G_{\infty} + N e_0 - T S(N, R) + E_{int}(N, R). \quad (2.1)$$

The first term, ΔG_{∞} , is the bare activation energy for the transition, that is, the energy required to form the “vacancy” and the “interstitial.” Until these two defects separate from each other, it will be energetically favorable for them simply to recombine; thus, especially at low temperatures, we need the string (or some other rearrangement of the surrounding molecules) to enable the system to reach a stable configuration. At high enough temperatures, ΔG_{∞} ought to become the ordinary Arrhenius activation energy.

The remaining terms on the right-hand side of Eq.(2.1) describe the string. e_0 is the energy per unit step along it. $S(N, R)$ is its entropy, which we obtain by computing the

number of random walks of N steps extending a distance R . In the limit of large N , the number of such walks, say $W(N, R)$, is approximately

$$W(N, R) \approx \text{constant} \times q^N \exp \left(-\frac{R^2}{2N\ell^2} \right), \quad (2.2)$$

where q is the number of choices that the walk can make at each step. Thus,

$$S(N, R) \approx \nu k_B N - k_B \frac{R^2}{2N\ell^2}; \quad \nu = \ln q. \quad (2.3)$$

The last term in Eq.(2.1), $E_{int}(N, R)$, is a repulsive interaction energy that accounts for the fact that no two pieces of the string can occupy the same position at the same time. This part of the analysis resembles Flory's calculation of excluded-volume effects in polymers. [22, 23] Following Flory, we assume that $E_{int}(N, R)$ is approximately the square of the string density integrated over the volume occupied by the string. Therefore, using Flory's mean-field approximation, also in the limit of large N , we write

$$E_{int}(N, R) \approx k_B T_{int} \frac{N^2 \ell^d}{R^d}, \quad (2.4)$$

where $k_B T_{int}$ is a repulsive energy (which contains dimensionless geometric factors) and d is the dimensionality of the space in which this string exists. As we shall argue, it is not necessarily true that $d = 3$.

Combining these terms, we have

$$\frac{\Delta G(N, R)}{k_B} \approx \frac{\Delta G_\infty}{k_B} - \nu N (T - T_0) + T \frac{R^2}{2N\ell^2} + T_{int} \frac{N^2 \ell^d}{R^d}, \quad (2.5)$$

where $T_0 \equiv e_0/(\nu k_B)$. The activation barrier is a saddle point in the N, R plane. That is, it is a minimum of $\Delta G(N, R)$ as a function of R and a maximum as a function of N . More explicitly, the two R -dependent terms have a minimum at $R = R^*(N, T)$, where

$$[R^*(N, T)]^{d+2} \propto \frac{N^3}{T}, \quad (2.6)$$

which is the Flory expression for the swelling of a d -dimensional polymer chain. Inserting this result into the R -dependent terms in (2.5), we find that the activation energy has the following form as a function of N :

$$\Delta G^*(N) = \Delta G(N, R^*) \approx \Delta G_\infty + \text{constant} \times T^{d/(d+2)} N^{(4-d)/(d+2)} - \nu N k_B (T - T_0). \quad (2.7)$$

The second term on the right-hand side is positive and, for $1 < d < 4$, is dominant for small enough N ; the third term dominates at large N . For $T > T_0$, the activation energy goes through a maximum at $N = N^*(T)$, where

$$N^*(T) \propto \left[\frac{T^{d/(d+2)}}{(T - T_0)} \right]^{\frac{d+2}{2(d-1)}}. \quad (2.8)$$

As in conventional nucleation theory, this fluctuation most probably will collapse for $N < N^*$, but will grow without bound if N becomes larger than N^* . Thus the activation energy $\Delta G^*(T)$ is the value of $\Delta G(N)$ at its maximum, that is,

$$\Delta G^*(T) = \Delta G(N^*, R^*) \approx \Delta G_\infty + \text{constant} \times \frac{T^{\frac{d}{2(d-1)}}}{(T - T_0)^{\frac{4-d}{2(d-1)}}}. \quad (2.9)$$

For the naively expected case of $d = 3$, these results are entirely unsatisfactory. The T -dependent factor in the activation energy, $T^{3/4}/(T - T_0)^{1/4}$, has too weak a divergence to be consistent with experimental data. Moreover, the energy scale is wrong. The implicit picture is one in which the string consists of a chain of N monopolar, vacancy-like fluctuations, so that e_0 would be roughly equal to $\mu \ell^3$, where μ is the shear modulus and ℓ is the molecular length scale introduced previously. Such an energy would be of the order of an electron volt, and would correspond to a temperature T_0 in the range of $10^4 K$ – too large for our purposes by about two orders of magnitude.

An apparently more plausible picture, and one which pertains specifically to the molecular structure of glassy materials, emerges from the concept of “frustration-limited domains,” introduced by Kivelson *et al.* [24, 25]. Their idea is that, in a glass-forming material, the energetically preferred structure of small clusters of the constituent molecules is one that cannot tile an infinite space. That is, the energetically favorable short-range order is “frustrated” because it cannot extend over long distances. Thus a quenched glass may consist of many domains, inside of which the molecules have arranged themselves so as to have their preferred local coordinations – or some approximation thereto; but these coordinations are violated on the interfaces between the domains. Accordingly, we speculate that the STZ activity is localized on a network of two-dimensional interfaces that separate the domains. In addition to giving us a rationale for choosing $d = 2$ in the preceding analysis, this hypothesis allows the energy e_0 to be much smaller than before, because the fluctuations are occurring in regions where the molecules already are more loosely bound to each other than they are within the bodies of the domains.

Choosing $d = 2$ and restoring missing constants, we write Eqs. (2.6), (2.8), and (2.9) as follows:

$$[R^*(N, T)]^2 \approx \left(\frac{2T_{int}}{T}\right)^{1/2} \ell^2 N^{3/2}; \quad (2.10)$$

$$N^*(T) \approx \frac{1}{2\nu^2} \frac{T_{int} T}{(T - T_0)^2}; \quad (2.11)$$

and

$$\frac{\Delta G^*(T)}{k_B} \approx \frac{\Delta G_\infty}{k_B} + \frac{T_{int} T}{2\nu(T - T_0)}. \quad (2.12)$$

Apart from the extra factor of T , Eq.(2.12) looks much like the Vogel-Fulcher formula with a linear divergence at $T = T_0$. Thus, we know from earlier analyses [25, 26, 27] that Eq.(2.12) will agree with experimental data near the glass temperature.

III. TRANSITION TO LIQUID-LIKE BEHAVIOR

The extra factor of T in Eq.(2.12), however, means that this formula predicts an excess, Arrhenius-like activation energy $k_B T_{int}/2\nu$ in the limit $T \rightarrow \infty$. (The situation is worse in three dimensions, where the activation energy grows like $T^{1/2}$ at high temperatures.) This physically unrealistic high-temperature behavior is a result of the fact that our large- N , mean-field approximations for the interaction energy and the entropy fail in the limit of small N . In this limit, the string disappears and the interaction energy should vanish accordingly; but our approximation says that the ratio N^2/R^2 in Eq.(2.4) goes to a constant. Note that the failure of the large- N approximation, by definition, occurs at the same temperature where the system switches from super-Arrhenius to simple Arrhenius behavior, and that this transition region is apparently where the system also switches from solid-like to liquid-like. Thus, in order to correct this unphysical feature of our results, we must confront the challenge mentioned in the Introduction – that is, we must try to construct a model of the transition between solid-like and liquid-like glasses.

As a first step in this investigation, we considered the possibility that a simple, *ad hoc* change in our expressions for the interaction energy and entropy might solve the small- N problem. Specifically, we corrected the interaction energy by noting that the number of interacting pairs of string elements is proportional to $N(N - 1)$ rather than just N^2 . There is no such simple correction for the entropy, however, because $S(N, R)$ is not a smooth function of its arguments near $N = 1$. In order to test the potential relevance of a small- N

correction, we simply enforced the correct behavior at $N = 1$ by multiplying our previous expression for $S(N, R)$ by $(N - 1)/N$. Our resulting activation energy did, in fact, approach ΔG_∞ at large T , but it did so over much too large a range of temperatures to agree with experiment. This should not be surprising. We have every reason to believe that there is new physics involved in the transition from solid-like to liquid-like behavior, and that this new physics should become apparent in the form of a new energy scale or an equivalent physical parameter.

The picture of a solid-like glass as a three dimensional mosaic of frustration-limited domains is appealing in several respects. Most relevant to our considerations is the idea that these domains are large and well defined in the super-Arrhenius region, and that their characteristic size, say $L(T)$, decreases with increasing temperature and vanishes as the system becomes liquid-like and its relaxation rates become simple Arrhenius. In our $d = 2$ approximation, we assumed that the critical excitation occupied a flat, interdomain region whose linear extent R^* was always much smaller than $L(T)$. We now relax that assumption and examine the possibility that the $d = 2$ approximation loses its validity as the temperature increases and that the critically long string – the one that determines the activation barrier – becomes three dimensional.

The assumption of a temperature dependent $L(T)$ leads us to guess that a significant part of the residual entropy of the glassy state resides in the relatively disordered interfaces between the domains. In that case, the entropy per unit volume contains a term that scales like $L(T)^{-1}$. Thus, if the entropy appears to extrapolate to zero at some non-zero Kauzmann temperature, then the extrapolation of $L(T)$ would diverge at that temperature. (We say “appears” because there may be no way, even in principle, to know whether that divergence of length and time scales actually occurs.) If we further assume that the Kauzmann temperature is the same as our T_0 , that is, the point at which relaxation becomes infinitely slow, then we might postulate that $L(T) \propto (T - T_0)^{-p}$. Here, p is some exponent that might be derived from first principles (which we wish we could do) or else be deduced from experimental data (which we shall try to do later in this paper). We must understand that the power law ceases to be valid above some temperature where $L(T)$ becomes smaller than the molecular length scale ℓ . At that point, the entropy levels off at a liquid-like value, signalling the upper edge of a specific-heat spike associated with an idealized glass-forming anomaly.

When $L(T)$ decreases so as to be comparable to or smaller than R , then the random walk followed by the string has the possibility of moving out of its original plane, and the interaction volume needed in the Flory-like analysis becomes ellipsoidal. Suppose that a walk of N steps extends a distance R in the plane and a distance $\pm Z$ in the perpendicular direction, so that the interaction volume (again, up to geometric factors that we absorb into the energy $k_B T_{int}$) is

$$\Omega_{int} = R^2 (\ell^2 + Z^2)^{1/2}. \quad (3.1)$$

To make a rough estimate of the number of walks in this volume, we note that the probability that any step in the original plane finds itself at the intersection between two domain boundaries is proportional to $\ell/L(T)$; thus we guess that a suitable generalization of Eq.(2.2) might be

$$W(N, R, Z) \approx \text{constant} \times q^N \exp \left[-\frac{R^2}{2 N \ell^2} - \frac{L(T) Z^2}{4 N \ell^3} \right]. \quad (3.2)$$

The factor 4 in the second term in square brackets restores spherical symmetry in the case $L(T) = \ell$. The small- N corrections will be negligible in what follows, and therefore we shall omit them. Our resulting generalization of Eq.(2.5) is:

$$\begin{aligned} \frac{\Delta G(N, R, Z)}{k_B} &\approx \frac{\Delta G_\infty}{k_B} - \nu N (T - T_0) \\ &+ \frac{T R^2}{2 N \ell^2} + \frac{T L(T) Z^2}{4 N \ell^3} + \frac{T_{int} N^2 \ell^3}{R^2 (\ell^2 + Z^2)^{1/2}}. \end{aligned} \quad (3.3)$$

The next step is to minimize $\Delta G(N, R, Z)$ with respect to R and Z for fixed N . There are two stationary solutions: one with $Z^2 > 0$, which we call the “three-dimensional” case, and another with $Z = 0$, which is the same as our earlier “two-dimensional” solution. Only one of these is actually a minimum of $\Delta G(N, R, Z)$ in the R, Z plane. In the three-dimensional case, the stationary point occurs at

$$\left[\frac{R^*(N)}{\ell} \right]^5 = \frac{2 T_{int} N^3}{T} \left(\frac{L(T)}{\ell} \right)^{1/2}; \quad (3.4)$$

$$\frac{[\ell^2 + Z^{*2}(N)]^{1/2}}{\ell} = \left(\frac{2 T_{int} N^3}{T} \right)^{1/5} \left(\frac{\ell}{L(T)} \right)^{2/5}; \quad (3.5)$$

and

$$\frac{1}{k_B} [\Delta G_3^*(N) - \Delta G_\infty] \equiv \frac{1}{k_B} [\Delta G(N, R^*, Z^*) - \Delta G_\infty]$$

$$\approx -\nu N (T - T_0) + \frac{5}{2} \left[\frac{T_{int}^2 T^3 N L(T)}{8 \ell} \right]^{1/5} - \frac{T L(T)}{4 N \ell}. \quad (3.6)$$

In the two-dimensional case, Eq.(2.10) remains the analog of Eq.(3.4), and

$$\frac{1}{k_B} [\Delta G_2^*(N) - \Delta G_\infty] \approx -\nu N (T - T_0) + (2 T T_{int} N)^{1/2}. \quad (3.7)$$

The function $\Delta G_3^*(N)$ always lies below $\Delta G_2^*(N)$ except at $N = N_c(T)$,

$$N_c(T) = \left[\frac{T L(T)^2}{2 T_{int} \ell^2} \right]^{1/3}, \quad (3.8)$$

at which point $\Delta G_3^*(N_c) = \Delta G_2^*(N_c)$ and the functions have equal slopes. The true minimum of ΔG for fixed N occurs on the two-dimensional branch ($Z = 0$) for $N < N_c$ and on the three-dimensional branch ($Z \neq 0$) for $N > N_c$; therefore there is a crossover between the two and three dimensional branches at the temperature T_c where $N_2^*(T_c) = N_c(T_c)$, with $N_2(T)$ being given by Eq.(2.11). That is, the crossover temperature is the solution of the equation:

$$\left[\frac{2 L(T_c)}{\ell T_c T_{int}^2} \right]^{2/3} \nu^2 (T_c - T_0)^2 = 1. \quad (3.9)$$

We are now ready to compare this theory with experimental data, first with the measurements reported in [28, 29, 30, 31] for the structural glass ortho-terphenyl, and second for the data reported in [32, 33] for the bulk metallic glass $\text{Zr}_{41.2} \text{Ti}_{13.8} \text{Cu}_{12.5} \text{Ni}_{10} \text{Be}_{22.5}$. In both cases, the experimental points that we show were obtained by deducing a temperature-dependent activation energy from viscosity measurements, that is, by fitting the measured Newtonian viscosity $\eta_N(T)$ to the function $\eta_0 \exp(\Delta G^*(T)/k_B T)$. The theoretical analysis in [4] implies that this procedure is equivalent to measuring $\Delta G^*(T)$ up to slowly varying logarithmic corrections.

The case of the structural glass is shown in Fig.1. We have taken the value $\Delta G_\infty/k_B = 3150 K$ directly from [31]. The low-temperature (two dimensional) part of the theoretical curve is shown as a dashed line for which the fitting parameters are $T_0 = 220 K$, $T_{int} = 1600 K$, and $\nu = \ln 4$. The high-temperature part is shown by the dot-dashed curve. As suggested above, we write

$$L(T) = \ell \left(\frac{T_1 - T_0}{T - T_0} \right)^p; \quad (3.10)$$

where T_1 is the temperature at which $L(T) = \ell$. Along with the preceding values of T_0 , etc., we choose $p = 15$ and $T_1 = 295$. The inset shows the crossover between these two curves

in detail and marks the crossover temperature, $T_c \cong 265\text{ K}$, obtained from Eq.(3.9). Figure 2 shows the critical string size $N^*(T)$ for the same parameters used in Fig.1, and shows separately the low-temperature (dashed curve) and high-temperature (dot-dashed curve) approximations. Note that, on the high-temperature curve, $N^*(T) = 1$ at $T \cong 350\text{ K}$, which is roughly the temperature at which the super-Arrhenius region ends. We also see at the crossover between the curves that $N^*(T_c) \cong 50$, which means that this crossover occurs within the large- N region of the theory.

We show the analogous data for the metallic glass in Fig.3, with the same conventions as in Fig.1. In this case, we have taken the experimental points from the viscosity data shown in [32, 33] and have converted them ourselves to values of $\Delta G^*(T)/k_B$. To perform this conversion, we first fit the high-temperature part of the data – above $T \cong 900\text{ K}$ – with $\eta_N \cong \eta_\infty \exp(\Delta G_\infty/k_B T)$; we find $\eta_\infty = 1.78 \times 10^{-10}$ and $\Delta G_\infty = 24300\text{ K}$. We then follow the procedure described in [31] and plot $T \log(\eta/\eta_\infty)$ as a function of the temperature. We again use $\nu = \ln 4$ and find $T_0 = 515$ and $T_{int} = 2800$. There is substantial uncertainty about the value of $\Delta G_\infty/k_B$ here, because it is not clear whether some crystallization or diffusive segregation of the constituents might have occurred in this multicomponent material at higher temperatures. Moreover, we do not have a continuous set of points spanning the high- and low-temperature regimes. Parameters for the high-temperature part were $p = 15$ (as before) and $T_1 = 750$. It is interesting to note, however, that most of the deformation measurements reported in [33] and discussed in [3, 4] were made in the low-temperature regime, where our two-dimensional curve, which does not involve $L(T)$, fits the data quite well. Figure 4 is the analog of Fig.2, showing $N^*(T)$ in the two different approximations. Again, the crossover occurs within the large- N regime.

IV. CONCLUDING REMARKS

We believe that the analysis presented here has some strong, intuitively appealing features. There also are places where, in order to obtain agreement with experiment, we have had to stretch our physical intuition in ways that will need to be reconsidered.

Our strongest assertion is that, in the spirit of Adam and Gibbs [17], the super-Arrhenius rates are truly nonequilibrium phenomena. That is, they describe transitions between near-equilibrium, inherent states and not, as sometimes has been assumed, an equilibrium distri-

bution associated with the states themselves. For example, it is assumed in [6, 12, 13, 14] that the equilibrium density of flow defects has a Vogel-Fulcher form. The model developed by Cohen and Grest [20] attributes super-Arrhenius behavior to percolation of liquid-like regions in equilibrated states. On the other hand, our nonequilibrium interpretation emerges naturally from the recent STZ theories [3, 4], where the equilibrium distribution of STZ's is purely Boltzmannian, and the super-Arrhenius behavior appears only in the thermally assisted fluctuation rate. We expect that this feature of our model, and its implication that the anomalous rates must derive from some multi-particle thermally activated process, will survive in later versions of this theory.

Our string model of the activation mechanism seems to us to be plausible enough to be taken seriously. We have not yet succeeded in finding a better alternative. Its biggest drawback is the fact that its simplest three-dimensional version is so obviously incorrect; the inverse $1/4$ power law in Eq.(2.9) seems completely inconsistent with experiment. Thus we have been led to adopt a more literal picture of frustration-limited domains than seems comfortable to us. This picture may be correct at low temperatures, where it produces the familiar Vogel-Fulcher result; and its success may even provide support for the existence of these zones in solid-like glassy systems.

On the other hand, the crossover to liquid-like behavior at higher temperatures, controlled by the scale length $L(T)$ for frustration-limited domains, is far less compelling. In the first place, our approximation for the entropy in Eq.(3.2) is at best a crude estimate of the number of string configurations on the three-dimensional, multiply connected, array of domain interfaces. More importantly, as we remarked in the Introduction, this intrinsically solid-like picture must lose its validity as the temperature increases. The fact that we need such a large exponent, $p = 15$, to describe the temperature dependence of the domain size $L(T)$ leads us to believe that we are missing some important element of the physical situation here. Perhaps a better approach would be to try to join the low-temperature theory at a crossover to a liquid-like approximation such as some version of mode-coupling theory.

Acknowledgments

This research was supported primarily by U.S. Department of Energy Grant No. DE-FG03-99ER45762, and in part by the MRSEC Program of the National Science Foundation

under Award No. DMR96-32716. A. Lemaitre was supported by the NSF under grants DMR00-80034 and DMR-9813752, by the W. M. Keck Foundation, and EPRI/DoD through the Program on Interactive Complex Networks.

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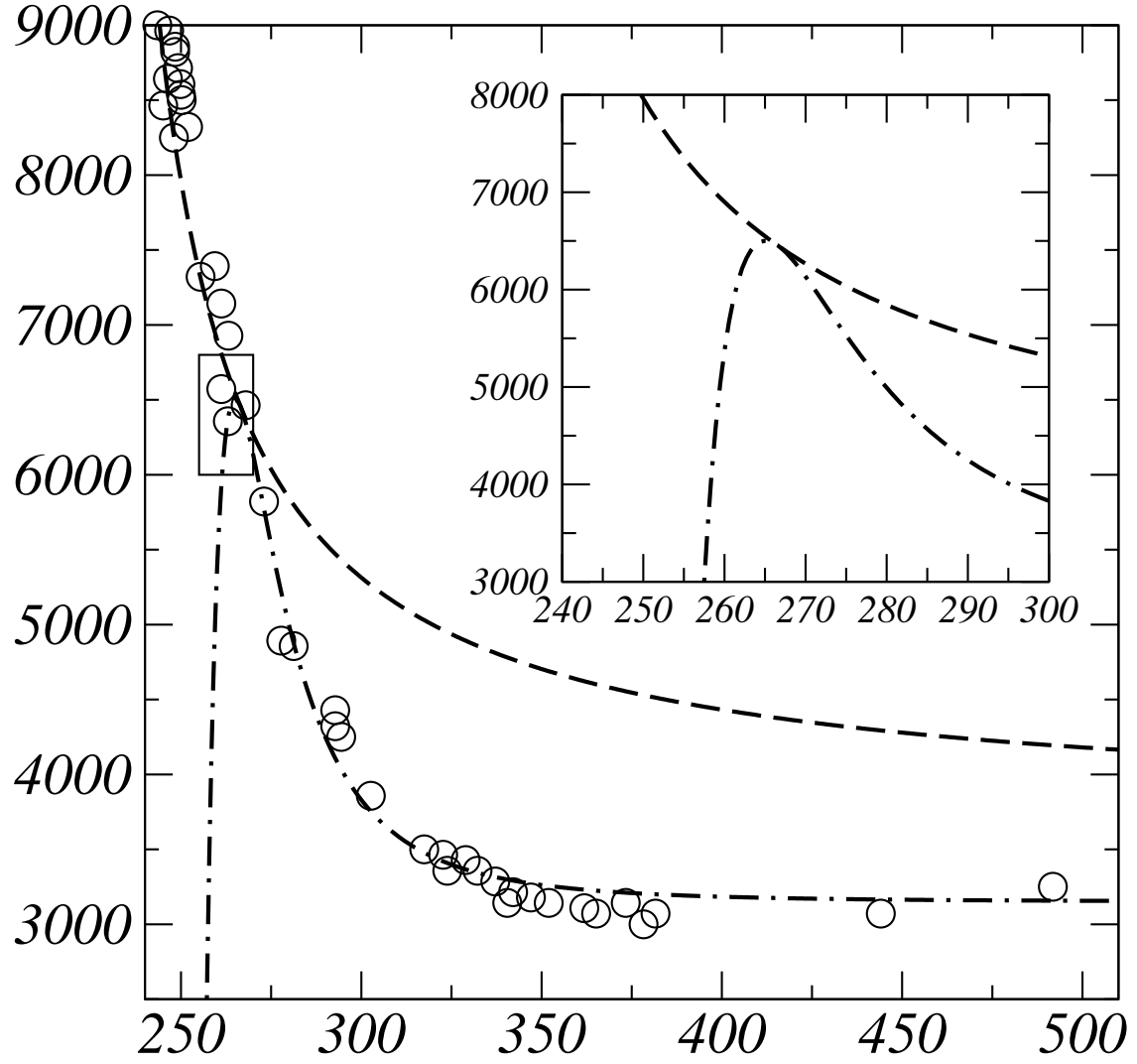


FIG. 1: Fits of ortho-terphenyl data from [28, 29, 30, 31]. The dashed line is a fit of the low temperature data with the theoretical curve from the two-dimensional theory (equation (2.12)). Parameters are $\Delta G_{\infty}/k_B = 3150$ K, $T_0 = 220$, $T_{int} = 1600$, and $\nu = \ln 4$. The dot-dashed line is the three dimensional expression (3.6) for the same parameters and, $p = 15$ and $T_1 = 295$. The complete theoretical curve lies on the dashed line at low temperature and on the dot-dashed line at higher temperature. The cross-over occurs at a temperature $T_c \sim 265$ K.

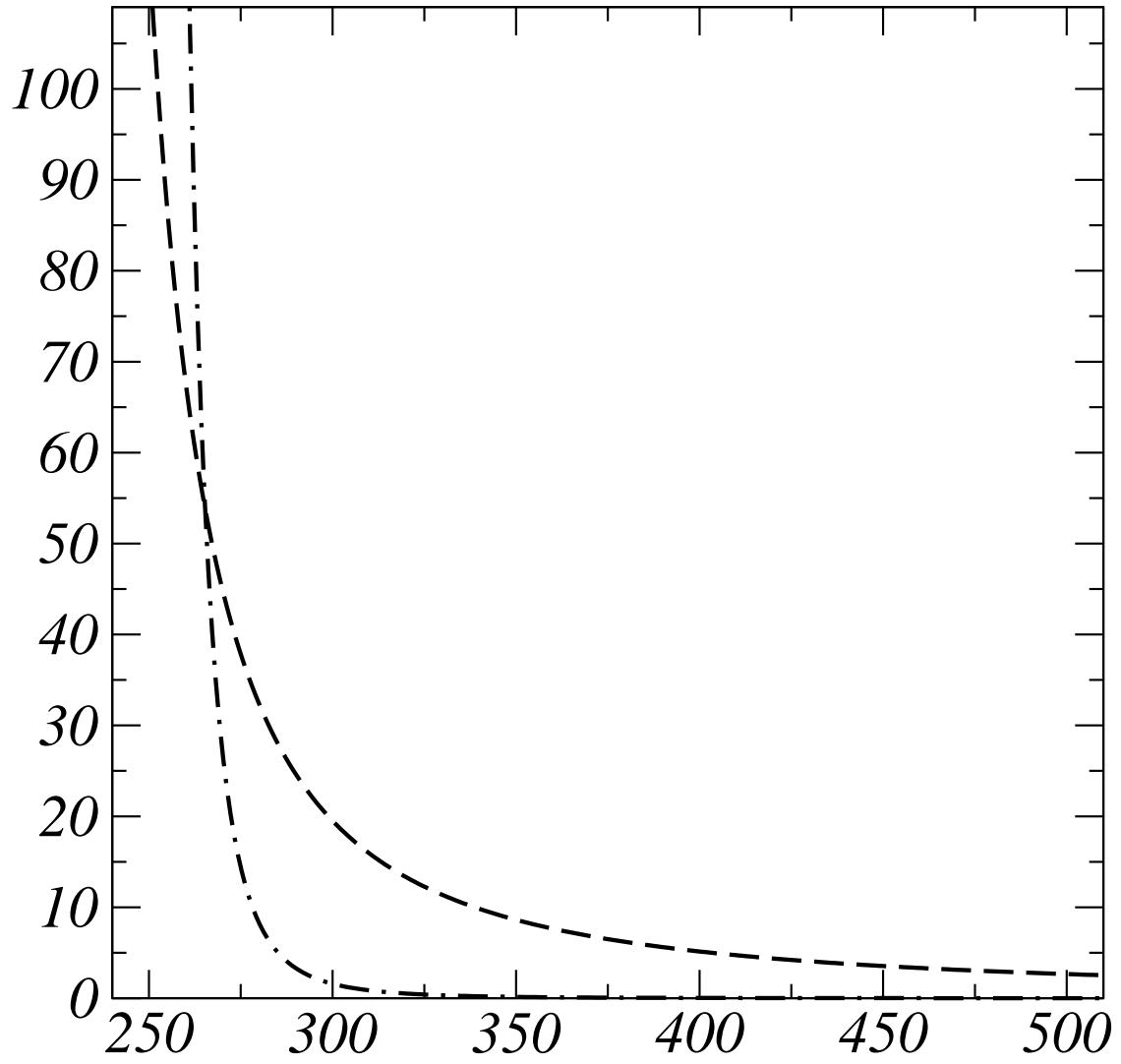


FIG. 2: Values of N^* for the two-dimensional (low-temperature) theoretical curve (dashed) and for the three-dimensional (high-temperature) theoretical curve.

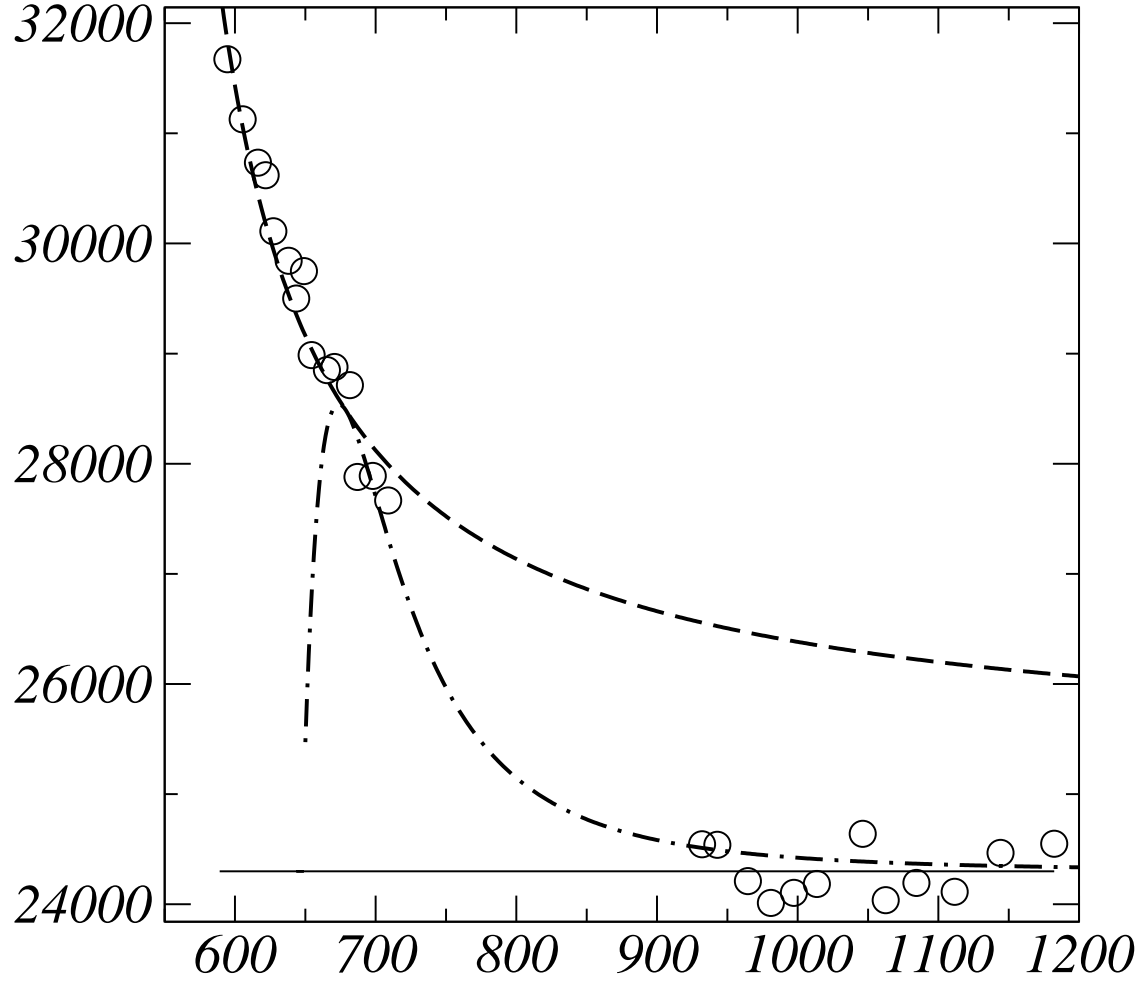


FIG. 3: Fits of metallic glass data from [32, 33]. The dashed line is a fit of the low temperature data with the theoretical curve from the two-dimensional theory (equation (2.12)). Parameters are $\Delta G_\infty/k_B = 24300 K$, $T_0 = 515$, $T_{int} = 2800$, and $\nu = \ln 4$. The dot-dashed line is the three dimensional expression (3.6) for $p = 15$ (as before) and $T_1 = 750$.

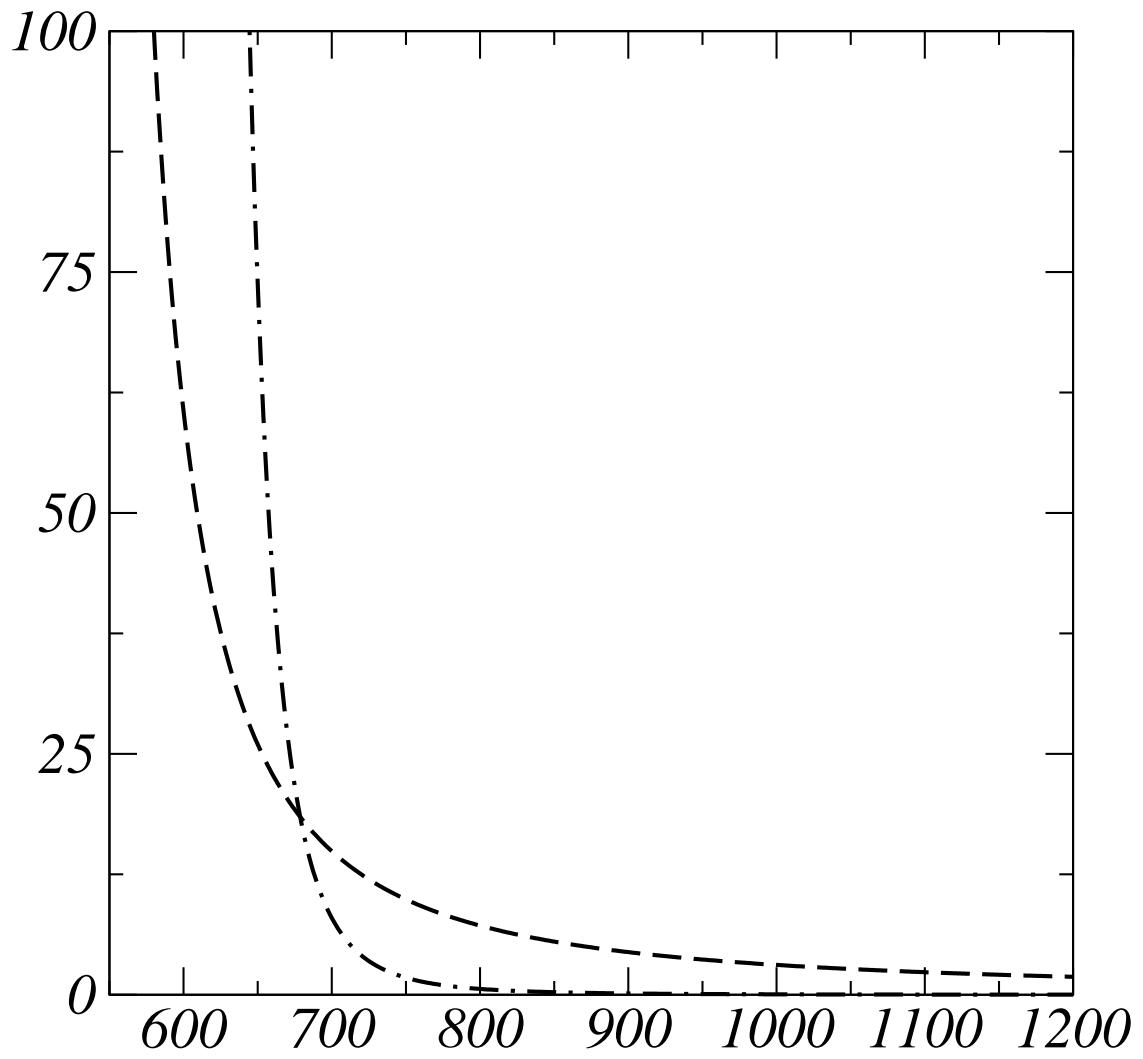


FIG. 4: Values of N^* for the two-dimensional (low-temperature) theoretical curve (dashed) and for the three-dimensional (high-temperature) theoretical curve.